On the constituents of the rhizome

of

Asarum Canadénse, Linn.

INAUGURAL DISSERTATION

submitted to the

Mathematical and Natural Science Faculty

of the

KAISER WILHELM UNIVERSITY STRASSBURG

for the

Acquisition of the Doctorate

by

FREDERICK B. POWER

of Hudson, N. Y.

Assistant at the Laboratory of the Pharmaceutical Institute.

STRASBOURG

TYPOGRAPHIE & LITHOGRAPHIE A. DUSCH

1880

96

On the constituents of the rhizome

of

Asarum Canadénse, Linn.

INAUGURAL DISSERTATION

submitted to the

Mathematical and Natural Science Faculty

of the

KAISER WILHELM UNIVERSITY STRASSBURG

for the

Acquisition of the Doctorate

by

FREDERICK B. POWER

of Hudson, N. Y.

Assistant at the Laboratory of the Pharmaceutical Institute.

STRASBOURG

TYPOGRAPHIE & LITHOGRAPHIE A. DUSCH

1880

Digitized by the Internet Archive
in 2026

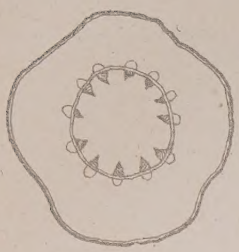
https://archive.org/details/IA41552714_0091

The chemical investigations contained in this essay were commenced at the Laboratory of Prof. Dr. **R. Fittig**, and were continued and brought to completion at the Laboratory of Prof. Dr. **F. A. Flückiger.**

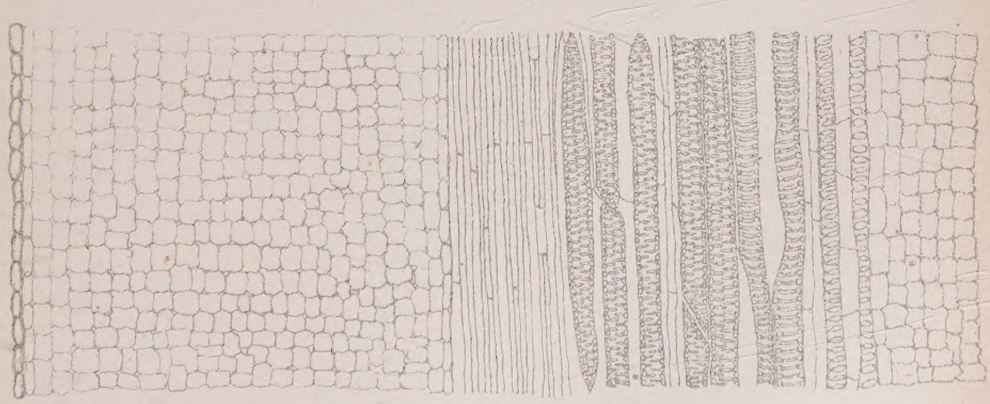
To my honored teachers, and particularly to Prof. **Flückiger,** I desire here to give expression to my thanks and gratitude, for uninterrupted kindness during my academic studies.

B

A

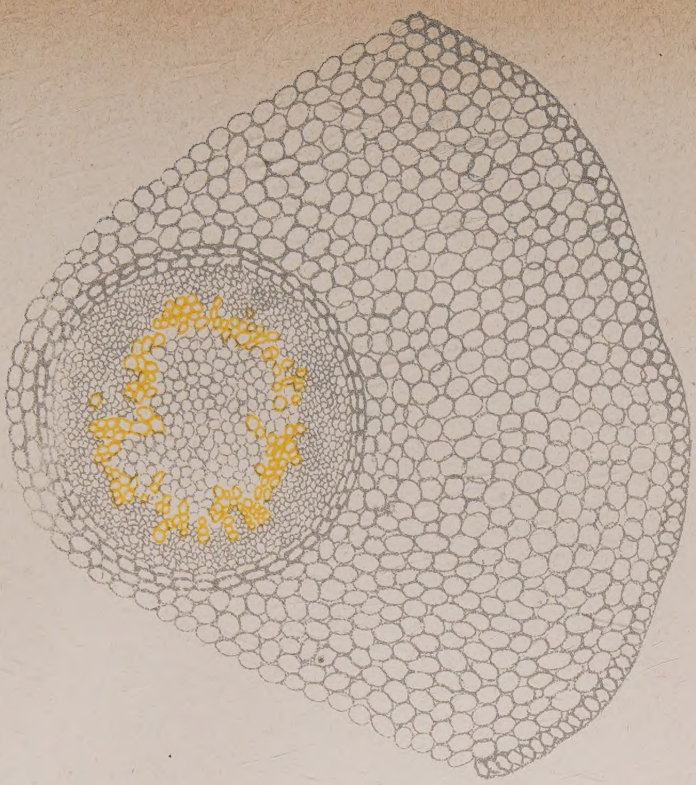


C

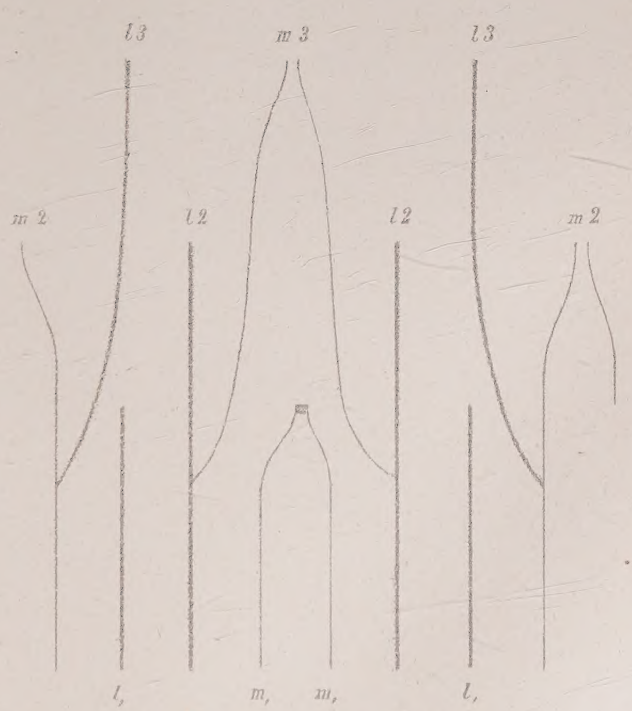


F.B.Power, del.

D



E



F.E. Power del.

On the constituents of the rhizome

of

Asarum Canadénse, Linn.

The subject to which this essay is devoted is one by no means new to pharmacologists; and although having from time to time attracted the attention of a few investigators in America, who have briefly noted its principal proximate constituents, we have still remained uninformed as to the true chemical nature of those substances which combine to form one of the most interesting of american plants. The object, therefore, of these researches, is to furnish a contribution to the Chemistry of American Materia Medica, and with the hope that the results attained may serve as a slight exponent of the richness of a field of research, as yet so comparatively untrodden and unexplored.

For the purpose of completeness, a brief summary of the botanical literature, and characters of the plant under notice may here be given; although the morphological structure of the same has already been long known, and has been carefully studied by botanists. The following specific characters are abstracted from Torrey's «Flora of the State of New-York», II. 1843, p. 131.

Asarum canadense, Linn. Nat. Ord. — Aristolochiàceæ Synonyms: Wild Ginger; Canada Snake-root; Coltsfoot; Canadian Asarabacca. «Rhizome about the thickness of a goose quill, branching, jointed, throwing out numerous fibrous roots. Leaves, usually two, at the extremity of each

branch, spreading 2—4 inches long, the breadth somewhat greater thau the length, very obtuse, or sometimes with a blunt point, pubescent on both sides : petioles 4—8 inches long, hairy. Flower on a peduncle about an inch long, often partly buried in the ground or concealed by dead leaves. Calyx dull purplish brown internally, woolly and yellowish green externally; the tube closely adhering to the ovary : limb deeply 3 parted; the lobes broad, with a slender acumination; the margins and finally the lobes also revolute, Stamens about the length of the style : filaments broadly linear, smooth ; anther cells oblong, distinct ; the subulate point of the connective produced beyond the cells, Stigmas linear-oblong, purplish, recurved, capsule ovoid, woolly crowned with the calyx lobes. Seeds ovoid, with a large fleshy raphe. Shady woods, in rich soil. *Fl.* May. *Fr.* July.»

For more detailed descriptions, as also for figures of the plant, the reader is refered to the following works.

Torrey, Flora of New-York, II, p. 31, tab. 92.

De Candolle, Prodromus, 15. I; Mich., Fl., Bor. Am., VI, p. 279.

Willd, Sp. Pl., v. 2, p. 838; Lamarck, Ill, t. 394, f. 2; Pursh, Fl. N. Am., v. 2, p. 596; Bigelow, Amer. med. Bot., I, p. 149, t. 15; Sweet, Brit. Flow. Gard I, tab. 95; Loddiges, Bot. Cab, t. 889; Bot. Mag., tab. 2769; Spreng. Syst., Veget, v. II, p. 461.

The synonyms, which at the present time are frequently attached to the american plant, may receive the following explanation.

Wild Ginger, on account of its aromatic properties, which were supposed to resemble those of ginger, and for which it was formerly often employed as a substitute.

Canada Snakeroot, from the similarity of its properties to those of Aristolochia serpentaria, which is also in turn known as Virginia Snakeroot.

Coltsfoot, probably in allusion to a similarity in the Shape of the leaf.

Asarum canadense presents but few prominent botanical distinctions from is congener, A. europæum, and indeed some botanists have considered them as simply varieties of one and on the same species. The two plants may however be readily distinguished from each other. A canadense is much more pubescent, the flowers of a brighter hue, and the rhizome usually attains a considerably larger size than the european species. There are also minor distinctions in the anatomy of the flower, as has been pointed out by H. Baillon, in Adansonia pp. 55—57, in his paper entitled, «Remarques sur l'androcée des Asarum et sur des appendices qui tiennent la place des pétales dans l'A. europæum.»

The most important difference however between the two species seems to be in the nature of their chemical constituents; the rhizome of A. europæum, according to several competent observers, possessing acrid, emetic, and cathartic properties, and was considerably employed in Europe previous to the introduction of ipecacuanha; white experience has demonstrated the american species to possess simply a mild, stimulating, and diaphoretic action, producing nausea only in large doses.

These differences in therapeutic action, however, may be possibly one of degree, rather thau of kind, as we shall consider hereafter.

The historical facts connected with our plant are by no means extended, and present but little of special interest.

It appears to have been cultivated by Bishop Compton in England prior to 1713, and was recommended as deserving a place in every collection on account of the peculiar structure of the flower.

Schöpf, a physician to german troops during the re-

volutionary war, who made some collections of american plants during his sojourn, the short descriptions of which were published a few years later in the small work entitled, «*Mat. Med. Americana*», Erlangæ 1787, mentions Aristolochia serpentaria, but seems not to have met with Asarum.

The generic application of the word Asarum, Ἄσαρον, seems to have originated with Dioscorides, and is mentioned by Mattioli in his «*Commentarii* in sex libros Pedacii Dioscoridis Anazarbei de medica materia» published at Venice in 1565. According to Torrey, «Flora of the State of New-York», II, 1843, p. 131, the word is derived from the Greck *a*, not, and *seira*, a band; on account of its habing been rejected from the garlands of flowers employed by the ancients. The correctness of this derivation of the word seems however quite improbable, but as it bears but little of pharmacological interest, its further discussion may be properly left to the consideration and study of the philologist.

Meyer, in his «Geschichte der Botanik», III. Band, 1856, p. 409, in quoting the list of plants contained in the *Capitulare* of the Emperor Charlemagne (see *Pertz*, Monumenta Germaniæ historica, Legum, 1836, I, p. 186), which may be considered as embracing the first rudiments of the Flora Germanica in the middle ages, refers the there in mentioned *Vulgigina* (plural), otherwise usually termed *Vulgago*, to Asarum europæum; and, ibid. p. 524 in explanation of the doubtful plants contained in the Physics of the Abbess Hildegardis, the same author says of Asarum, «Asarum (31, 36) und Aserum 116 (123) kann dem davon gemachten Gebrauch nach nicht Asarum europæum sein, wie Reuss meint. Im Text von Cap. 31 wird Asarum sogar als herbula suavis bezeichnet, und unser Asarum kommt ausserdem unter seinem bekannten deutschen Na men Haselwurz, 95, vor, den Reuss unerklärt lässt. Ich

halte es für Glechoma hederacea, in den Glossen gewöhnlich Acer, Gundereba, in S 2, p. 21, Nr. 24, Acera. Die Synonyma, Helmstadiensia, unter A. 91, stellen Acer, Acera, Azarum, Edera terrestis zusammen und übersetzen Gundeleve oder Gundelrave (wo mein Codex Gondram, das jetzt gewöhnliche Gundram hat).»

The general characters of the rhizome are so well known, that a detailed description in this place would seem quite superfluous. It occurs in commerce either with the rootlets attached, or the same removed; the latter being the most select article, and is preferred for the manufacture of the volatile oil. It thus presents the form of somewhat contorted fragments, 3—6 inches in length, and about $^1/_6$—$^1/_8$ inch in diameter; the internodes being situated at distances of about $^1/_2$ inch from each other. The rhizome is of a light brown color, wrinkled longitudinally, and breaks with a short fracture. The taste is pungent, very aromatic, and slightly bitterish. The rhizome in a fresh condition has an odor reminding quite strongly of Patchouli.

The rhizome in its anatomical structure agrees quite closely with that of A. europæum; but not having been as yet either figured or described. I have considered it deserving of a microscopical examination, an opportunity of accomplishing which was afforded me at the botanical laboratory of Prof. De Bary. The material from which the sections represented by the drawings accompanying this essay were made, was obtained from a living plant, cultivated at the Botanical Garden of Strassburg.

Plate I, Fig. A. A cross section of the fresh rhizome, of about five times the natural size; showing the relation of bark and wood, and the arrangement of the vascular bundles.

Fig. B. A portion of a more highly magnified cross section of the rhizome. The epidermis consists of a single row of cells, the outer walls of which are of a brown color. The vascular bundles, usually about 12 in number, although

subject to slight variation, form an interrupted circle, and are traversed by a prominent cambium ring. The Xylem forms a group of wedge shaped vessels, the walls of which contain a deposit of yellow coloring matter. The parenchymatous tissue of the rhizome, both of the bark and medulla countains a large amount of starch in the form of simple spherical granules, and usually in groups of 2—4.

The parenchyma of the bark contains, in addition to the starch, some chlorophyll and resin, and numerous cells replete with volatile oil. These oil cells have been made the subject of special study by Dr. E. Zacharias, whose results have been elaborated in an article, entitled.

«Ueber Secret Behälter mit verkorktem Membran.» Bot. Zeitung, N° 40, 1879. The oil cells can not be distinguished in their form from the surrounding parenchyma, but show a marked difference in their behavior toward reagents; the cell membrane remaining undissolved by the action of concentrated sulphuric acid, and are further particularly characterized by the presence of two lamina, the inner consisting of cellulose, while the outer consists of suberous matter, and is colored brown by chloro-iodide of zinc.

Fig. C. A magnified longitudinal section of the rhizome, in a radial direction. The Xylem is seen to consist of spiral, ringed, scalariform and pitted vessels, between which are found a few isolated, thin walled, narrow ligneous cells. The Phloem or bast portion consists of sieve tubes, together with narrow extended cells in the cambiform tissue, some of which contain a brownish liquid, and whose walls show the reactions of cellulose.

Plate II. Fig. D. A magnified cross section of a rootlet. The epidermis consists of a row of angular or polyhedral cells, with brown colored walls. The central portion of the rootlet is composed of a group of irregularly scattered vessels, enclosing a small medulla, and surrounded by sieve

tubes and extended cells. The walls of the vessels contain, as in the rhizome, a yellowish or brownish yellow coloring matter. The entire central portion is enclosed by the endodermis, with its thickened lateral walls, connected with a row of alternating thin walled cells, which constitutes the pericambium.

Fig. E. This diagram represents the course of the vascular bundles in the rhizome; the letters m_1, m_2, etc., designating the median bundles, the letters l_1, l_2, etc., the bundles whose course is in a lateral direction, and from which it follows without further explanation that the number of vascular bundles observed on a cross section must naturally be subject to some variation.

Chemical examination of the rhizome.

The proximate chemical constituents of the rhizome at Asarum canadense appear to have first been briefly recorded by Bigelow, who ascertained the presence therein of volatile oil, resinous matter, starch and gum. Rushton[1] subsequently observed, in addition to the above mentioned substances, the presence of fatty matter, chlorophyll, salts of lime, potassa and iron, to which may be added lignin. Procter[2] afterwards called attention to the distinctive characters of the american and european plant, and quotes the results of the observations of Graeger, and Lassaigne and Feneulle, on the constituents of A. europæum. He further ascertained the absence of the so-called *Asarite,* or *Asarum camphor,* in the rhizome of A. canadense. Thirty five years after the publication of Procter's observations, attention was called by Van Gorder[3] to the rhi-

1. Amer. Journ. of Pharm., vol. X, p. 181.
2. Ibid., vol. XIII, p. 177—182.
3. Ibid., vol., 48, N° 4. 1876.

zome of A. canadense as an indigenous aromatic, but without any further development of our knowledge of its constituents. This short résumé of the literature upon the chemistry of our subject is believed to comprise all the hitherto developed facts, which are seen to be far from possessing that degree of repleteness which should be desired, or which modern science must demand.

An opportunity has been afforded me of devoting considerable time and study to the development of the chemistry of the subject under notice; the interesting results of which I shall here describe.

The volatile oil of Asarum europænm has never been the subject of any chemical investigation, and nothing more is therefore known of it than the so-called Asarum camphor. Asarit, or Asaron of the older writers. Of the composition of the aromatic volatile oil of Asarum canadense we have remained equally ignorant. The latter having recently attracted some attention, in consequence of its application in the art of perfumery, I have considered it worthy of careful analysis, and it is to this body that my attention has been chiefly directed, and confined.

Through the kindness of Dr. Squibb, of New-York, I have been provided with an amount of the carefully selected rhizome sufficient for all the purposes of experiment, and which has enabled me at the same time to examine the other constituents of the rhizome, independent of the volatile oil.

As has been previously observed, the rhizome contains an aromatic volatile oil, a large amount of starch and gum, together with a small amount of resin and fatty matter. In addition thereto may be mentioned an amorphous yellow coloring matter, readily soluble in water, and precipitable by basic acetate of lead. This coloring matter, which corresponds to the Asarin of Graeger, is a substance which appears to be widely distributed in plants. It assumes an

intense yellow coloration upon the addition of alkalies, and strikes a dark green coloration upon the addition of ferric salts, but apears not to belong to the class of true tannic matter, inasmuch as it is not precipitated by a solution of gelatine. The rhizome also contains a large amount of uncrystallizable sugar, which reduces cupric oxide even in the cold, and is particularly rich in nitrates, which crystallize from the alcoholic extract upon standing. I have submitted thirty pounds of the ground rhizome, to the action of boiling alcohol in a distillatory apparatus. The dark colored, concentrated, alcoholic liquid was poured into a large volume of water acidulated with acetic acid, in order to separate the volatile oil, resin etc. The aqueous liquid was then filtered, concentrated by evaporation, and the large amount of coloring matter completely precipitated by basic acetate of lead.

The filtered solution was then freed from lead by hydrosulphuric acid. By this treatment a bright liquid was obtained, possessing but a slight yellowish coloration, and which was again concentrated by evaporation on the water bath.

With the usually employed alkaloidal reagents, the solution thus obtained shows indications of the presence of a small amount of an alkaloid, which is interesting from the fact that no alkaloid has as yet been observed in the family of Aristolochiàceæ. The principle in question may be isolated by the following means. It is absorbed by ether from an alkaline solution, and may also be precipitated by tannic acid; the solution being maintained neutral by means of carbonate of sodium. As precipitated by tannic acid it forms a dense light brown precipitate, which is however readily redissolved by an excess, either of tannic acid or of alkali.

It may then be extracted from the tannic compound by the usual treatment with either carbonate or oxide of

lead, and alcohol. As obtained by either of these methods, it forms a dark colored, hygroscopic, resinous substance, of unpleasant odor, and slightly bitterish taste. The aqueous solution, when cautiously evaporated to dryness, is then with difficulty redissolved by water, and is perfectly neutral in it action upon litmus.

The solution shows the following behavior toward alkoloidal reagents:

I. *Mercurio-potassic iodide*, a colorless, flocculent precipitate, which soon aggregates to a compact resinous mass.

II. *Iodine in potassium iodide*, a reddish brown precipitate.

III. *Mercuric chloride*, a slight turbidity.

IV. *Auric chloride*, a slight turbidity.

V. *Tannic acid*, upon the addition of carbonate of sodium, a dense, light brown precipitate.

VI. *Platinic chloride*, a light yellow, crystalline precipitate.

This substance, if indeed an alkaloid, and to which the combined reactions, and more particularly the crystalline platinic compound would seens to point, must be a very feeble base, as it is destitute of alkaline reaction, and I have also been unable to detect the presence of nitrogen by Lassaigne's test.

Its amorphous character, and apparent inability to from any simple crystalline salts, render it quite impossible to obtain it in a form sufficiently pure for analysis, and which has not attracted me to its further investigation.

I have also had no opportunity of ascertaining whether it is possessed of any physiological action; although the supposition may be expressed that the active properties of the rhizome of A. europæum are due to a similar principle, and which may possibly be developed in the latter to a larger extent than in the american species.

The rhizome, when dried perfectly at 100° c., loses 17,10 % in weight; and then yields, when dried at this temperature, 13,43 % of ash, composed of silicic acid, carbonates, chlorides, sulphates and phosphates of potassium, sodium, calcium, magnesium, aluminium and iron.

Analysis of the volatile oil.

By far the most interesting and important constituent of the rhizome of Asarum canadense is the volatile oil, wihich has also been kindly furnished me at my request by Dr. Squibb, of New-York. It was obtained from material carefully selected by himself, and distilled in his own laboratory, so that the results of the experiments here detailed may be accepted as indicating the composition of a body, the authenticity and purity of which may be relied upon whit the utmost confidence. In the process of distillation no solid or crystalline bodies were found to be formed, either in the still, or in the distillate; nor did the latter furnish any crystalline body by exposure to cold, thus confirming the previous observations of Procter. Indeed, the Asarum camphor of Graeger, and Lassaigne, and Feneulle, is a substance of which we know but little, and of which the statements regarding its composition and properties are greatly at variance.

It seems, morcover, not to have been met with by any later observer, and Zeller, in his «Studien über die ätherischen Oele», Stuttgart 1855, remarks of Asarum europæum, that he could only obtain a liquid volatile oil, which after being preserved for *fifteen years* in half filled vessels, and exposed to severe cold, showed no tendency to crystaltization; also a water saturated with the oil, and containing oily particles, showed, after standing for several years, no separation of a camphor like body. He makes there from the deduction, that the camphor is not an hydrate of the

oil, but rather a stearoptene, which is only formed at an advanced period of the life of the plant, or by the drying and preservation of the same, from the therein contained oil.

Fifty pounds of the rhizome, with *rootlets attached,* yielded to Squibb about 18 ounces of volatile oil, corresponding to $1^{75}\,\%$. This oil is of a bright yellowish green color. Its specific gravity is 0,933 at 12,5° c. Its rotation in sodium light, in a column of 100 mm, is — 1°,3′, at 15° c.

Fifty pounds of the rhizome, with the *rootlets previously removed,* yielded to Squibb 25 ounces of volatile oil, or $3^{12}\,\%$. This oil is somewhat lighter in color thau the preceeding, and possesses also a finer odor. Its specific gravity is 0,942, at 12,5° c. Its rotation, in sodium light, in a column of 100mm, is — 2°, 4′, at 15 c.

A portion of ground rhizome afforded me upon distillation but $1^{15}\,\%$ of volatile oil. This small percentage, however, is probably due to the non-application of steam heat. The oil was of a bright lemon yellow color.

Its specific gravity at 17° c. is 0,953. Its rotation in sodium light, in a tube of 100mm, is—0°,6′ at 15°,5 c.

The recently dried rhizome afforded Procter the surprisingly large amount of $5\,\%$ of volatile oil, of a straw yellow color. Another specimen of the oil, which was kindly furnished me by Prof. Flückiger, and distilled by Schimmel and Co., of Leipsic, being also of known purity, was of a light amber color. Its specific gravity is 0,939, at 12,5° c. Its rotation, in sodium light, in a tube of 25mm, is + 0°,6′ at 15° c.

The behavior of the different specimens toward polarized light is thus seen to vary considerably, and cannot be accepted as a criterion of the purity of the oil.

The odor of the oils is highly and agreably aromatic, and characteristic of the rhizome from which they are obtained. Their action upon litmus was found to be quite

neutral, as also water which had been shaken with the oil, and allowed to remain in contact for some time. The oil, upon standing for a considerable lenght of time, however, gradually acquires an acid reaction.

The oil which I have employed for analysis, was that distilled for me by Dr. Squibb. It remains perfectly clear and liquid when exposed for some time to a temperature of — 27° c.

An attempt was first made to separate the constituents of the oil by fractional distillation, after having been previously dried over chloride of calcium, but, upon heating, the mercury suddenly rose to 190° c., and under 200° but a small fraction was obtained, which possessed a strongly acid reaction. This behavior pointed to the presence of compound ethers, and their separation proving impossible by direct distillation, the oil was saponified by treatment with alcoholic potassa. The proportions found to be most suitable for this purpose, were, oil 100 parts, potassium hydrate 15 parts, and commercial alcohol 200 parts. This mixture was heated for 8 hours in a water bath, in a flask provided with an inverted condenser, and the applied alcohol afterwards for the most part separated by distillation.

The alcohol, thus recovered, was largely diluted with water, forming a milky mixture, and after standing for some hours, a small amount of an oily liquid separated upon the over surface, which was removed, and added to the oil subsequently obtained by distillation. The contents of tthe flask, which were found to still remain strongly alkaline, were then largely diluted with water, and distilled; the operation being repeated, with successive additions of fresh portions of water, until no more oil drops passed over with the aqueous vapour. A colorless oil was thus first obtained, and finally a bluish colored oil, in small amount. From 750 grams of oil, saponified by this treatment, a pro-

duct was obtained amounting to 635 grams. This was then carefully dried, by being allowed to rest in contact with ignited carbonate of potassium for several days, and was then submitted to fractional distillation.

By means of a long continued and tedious process of systematic fractionation, extended through a period of several weeks, I finally succeedet in resolving the product into the following fractions, and having quite constant boiling points:

(I). — A small fraction distilling below 180° c., which after treament with metallic sodium, and subsequent rectification, gave a product distilling at 163—166° c. (Uncorr.).

The entire amount of this purified product was but 12 grams.

(II). — A product distilling at 195—198° c. (Uncorr.), 196^9—199^9° c. (Corr.), and amounting to 195 grams.

(III). — A product distilling at 220—223° c. (Uncorr.), 222^8—226° (Corr.), and amounting to 90 grams.

(IV). — A product distilling at 249—252° c. (Uncorr.), 254^3—257^5° (Corr.), and amounting to 210 grams.

(V). — An oil of an indigo blue color, possessing an empyreumatic odor, and which was collected from 275—350° c. The amount of this product was 40 grams.

Above this temperature but a small amount of tarry liquid was obtained, consisting chiefly of decomposition products; the residue in the fractionating vessel concreting upon cooling to a solid pitch like mass.

These several fractions were then made the subject of investigation and study.

I. Fraction 163—166° c. (Uncorr.).

This was submitted to analysis with the following result, 0,1925 gr. of substance gave 0,6166 gr. $CO_2 = 0{,}1681$ C, and 0,2102 gr. $H_2O = 0{,}0233$ H.

Calculated for $C_{10}H_{16}$			Found
C_{10}	120	88,24%	87,36%
H_{16}	16	11,76%	12,13%
	136	100,00	99,49

This fraction, which has an agreeable lemon like odor, is thus seen to consist simply of a terpene, but the small amount obtained would admit of but a limited number of experiments. Its specific gravity is 0,844 at 13° c., and is optically inactive, upon saturating it with dry hydrochloric acid gas it became deeply colored, and assumed a strong camphoraceous odor, but formed no crystalline compound. It also furnished no crystals of terpine by treatment with dilute nitric acid.

II. Fraction 196°—199° c. (Corr.).

This is a bright, colorlees and very fragrant liquid, reminding somewhat of coriander, and emitting when allowed to evaporate upon an extended surface a decided camphoraceous odour.

It was submitted to analysis with the following result:

I) 0,3733 gr. of substance gave 1,0635 gr. CO_2 = 0,2900 c., and 0,3981 gr. H^2O = 0,0442 H.

II) 0,2605 gr. gave 0,7545 gr. CO^2 = 0,2058 C, and 0,2765 gr. H_2O = 0,0307 H.

Calculated for $C_{10}H_{18}O$			Found	
			I	II
C_{10}	120	77,92%	77,68%	77,72%
H_{18}	8	11,69%	11,84%	11,78%
O	16	10,39%		
	154	100,00		

This fraction is seen to consist of a liquid modification of Borneo camphor or Borneol; a body which has been quite frequently met with in various volatile oils, such as the oil of hops, cajeput, coriander, Osmitopsis astericoides,

Pelargonium roseum, valerian, and, according to Wright[1], citronella oil is principally composed of a liquid, isomeric with borneol, white Gladstone assigns to the same body the formula of ordinary camphor. The composition of the oil is therefore possibly not constant, and Wright's results are further supported by the composition of several derivatives, Oil of lemon appears also to contain a small amount of an isomer of borneol in the form of an acetic ether, and the same may be said of the oil of wormseed, as obtained from the minute unexpanded flower heads of Artemisia maritima.

Another body isomeric with borneol has quite recently been obtained by Landolph[2] from Anethol; the latter yielding by oxydation with nitric acid, among other products Anethol camphor $C_{10}H_{16}O$, or considered as *Anethol tetrahydride* $C_6H_6\left\{\begin{matrix}O\,C\,H_3\\C_3\,H_7\end{matrix}\right.$.

This latter compound when heated for some time in sealed tubes with alcoholic potassa is converted by assumption of a molecule of hydrogen into $C_{10}H_{18}O$, or Anethol borneol, regarded by Landolphas *Anethol hexahydride,* and to have the constitution $C_6H_8\left\{\begin{matrix}O\,C\,H_3\\C_3\quad H_7\end{matrix}\right.$.

This compound is described as forming a clear, syrupy liquid at ordinary temperatures, and boiling at 198° c.

At 0° c. it crystallizes in long, radiating needles, which melt at 18—19° c. and has a peculiar penetrating, and disagreeable mouldy odour.

It is evident that if the constitution assigned by Landolph to this body be correct, that it is simply isomeric with borneol, not a modification of the same, and must consequently possess different properties, and show a diffe-

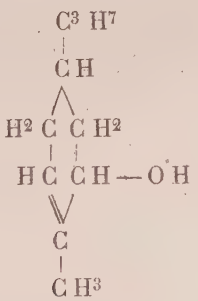
---

1. Journ. Chem. Soc., 1874, p. 318.
2. Ber. d. deutsch. Ch. Ges., 1880, p. 146.

rent chemical behavior; for while borneol possesses all the characters of a secondary alcohol, the socalled Anethol borneol must be regarded as a compound phenylic ether.

We are indebted to Berthelot[1] for the first recognition of the alcoholic nature of borneol; who says: «Le camphre de Bornéo joue le rôle d'un alcool: je le désignerai, pour abréger, sous le nom d'*alcool camphol*ïque ou *camphol*. C'est le premier exemple d'une série d'alcools monoatomiques représentés par la formule générale $C^{2n} H^{2n-2} O^2$ (According to present notation it should be written. $C^n H^{2n-2} O$). La fonction de ce principe naturel était demeurée inconnue jusqu'ici; je vais la démontrer par la formation directe de ses éthers stéarique, benzoïque et chlorhydrique.»

The constitution of borneol cannot as yet be regarded as definitely established, and different views are still entertained by chemists as to its structure (see Jahres-Bericht der Chemie. 1870, p. 625-626; ibid., 1872, p. 475; Ber. d. deutsch. ch. Ges., 1872, p. 1106). According to Kachler's view[2], it bears the same relation to ordinary camphor as isopropyl alcohol to acetone. The following formula, which has been assigned to it by Kekulé[3], and in which a closed benzol ring is accepted, is at present considered as the most probable.



1. Ann. de chimie et de physique. 1859, t. LVI, p. 78.
2. Liebig's Annalen, 169, p. 186.
3. Ber. d. deutsch. chem. Ges., 1873, p. 929.

In this formula the relative position of the methyl, and propyl or isopropyl groups, is considered by Kekulé as being definitely settled; for the oxygen atom, aud the double connection on the contrary, the relative position, as well toward each other, as also in relation to the two side chains, remains provisionally undecided.

Being in possession of a considerable quantity of this liquid isomer of borneol (which in acceptance of adopted nomenclature may be designated as *Asarol*), I have considered it of interest to institute a somewhat extended series of experiments.

Its rotation, in sodium light, in a column of 100 mm, is + 4°, 1′, at 15°,5 c. Borneol obtained by distilling amber with potash rotates + 4°, 5′; while Kachler[1] found sublimed borneol, dissolved in the proportion of 154 grams, or its molecular weight, in a litre of acetic ether, to rotate the plane of polarization + 12°, 0 at 20° c. in a column of 200 mm.

It retains its liquid condition when exposed for some time to a temperature of — 27° c.

A determination of its vapour density was made according to Dumas' method, with the employment of a paraffine bath; the factors thus obtained may be designated as follows:

m = The weight of the globe filled with air = 27,8186 gr.
m' = The weight of the globe filled with Asarol vapour = 28,1524 gr.
M = The weight of the globe filled with distilled water = 126,0860 gr.
t and b = The temperature of the vapour, and barometric pressure at the moment of sealing the globe, or 252° c., and 740 mm.

---

1. Liebig's Annalen, 197, p. 86.

t' and b' = The temperature of the balance case, and barometric pressure at the time of weighing the vapour, or 11° c., and 740 mm.

λ' = The density of the atmospere in relation to the temperature t', and barometric pressure $b' = 0{,}001210$.

Q = The density of the water with which the filled globe was weighed = 0,99943.

$3\,\beta$ = The cubical coefficient of expansion of glass, which is accepted as $\frac{1}{40{,}000}$.

Inserting these factors in the formula:

$$d = \left(\frac{m'-m}{M-m}\,\frac{Q-\lambda'}{\lambda'} + 1\right)\left(1-3\,\beta\,(t-t')\right)\frac{b}{b'}\,\frac{1+0{,}003665.t}{1+0{,}003665.t'}$$

we obtain for d the value *5,98;* or the vapour density of the Asarol deducted from atmospheric air at the temperature t, and barometric pressure b.

The calculated vapour density is *5,33;* thus proving the empirical formula assigned to the Asarol to be correct, and the somewhat higher value obtained being due to a slight decomposition or polymerization by the action of heat, as the vapour condensed in the globe was observed te be slightly colored, and somewhat denser thau the liquid originally employed.

Through the kindness of Mr Fock I was able to ascertain its *index of refraction*, the results of which as deduced from the well known formula $n = \dfrac{sin\left(\frac{1}{2}\,\delta + \frac{1}{2}\,\varphi\right)}{sin\ \frac{1}{2}\,\varphi}$

where n represents the index of refraction, may be tabulated as follows:

With Lithium light 1,4642
With Sodium light 1,4668
With Thallium light 1,4716

The temperature of the liquid was 17° c.

The specific gravity of the liquid is 0,8745 at 17° c.

From the index of refraction as above given with a sodium flame, the *specific refractive energy* may be deduced as follows, $\frac{n-1}{d}$ or 0,5338, where d represents the specific gravity of the liquid at 17° c. The *molecular refractive energy,* or *equivalent of refraction* is then *82,2;* being considerably higher than the calculated number *76,4*, in acceptance of the atomical refractive energy C = 5, H = 1,3, O = 3.

It has however been ascertained that this relation between the refractive energy and chemical composition of a body finds its full value only in compounds of the marsh gas series or those more diretly connected therewith, and containing a relatively small percentage of hydrogen atoms; while in compounds richer in carbon, the atomical refractive energy is considerably higher than the values here given, and is also dependent upon the grouping of the carbon atoms in the molecule. These values must then of necessity vary when we accept thal in the marsh gas series the carbon atoms form a chain, and in the aromatic series, or benzol derivatives, by alternating single and double union of the carbon atoms, a closed ring.

That the Asarol contained in the volatile oil of Asarum canadense is really an alcohol, and present in the form of a compound ether, I have also convinced myself.

This was indeed to be pre-supposed from the neutral character of the oil itself, its partial decomposition upon distillation, with separation of the acid, and by having proved the absence of alcohols of lower boiling points.

To prove its alcoholic nature I have formed therefrom an acetic ether. For this purpose the Asarol was mixed with acetic anhydride in such a proportion as to form acetic acid

with the molecule of water evolved by the reaction, or as formulated :

$$C_{10}H_{18}O + \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\rangle O = C_{10}H_{17}O(C_2H_3O) + C_2H_4O_2.$$

This mixture was heated upon the sand bath, and maintained in gentle ebullition for about six hours, and the product then fractionated. Owing to a partial decomposition by the continued action of heat, the process of fractionation could not be long continued.

I succeeded however in isolating two principal fractions, and having quite constant boiling points :

(1) 236 — 239° c. (Mercurial column entirely in the vapour).

(2) 239 — 242° c. (Mercurial column entirely in the vapour).

These fractions have a very agreeable odor, quite distinct from the Asarol, and remirding quite strongly of Pear.

They were both analysed with the following result :

I. (Fraction 236—239° c.) 0,2314 gr. of substance gave 0,6198 gr. CO_2, = 0,1690 C, and 0,2156 gr. H_2O = 0,0239 H.

II. (Fraction 239—242° c.) 0,1582 gr. of substance gave 0,4246 gr. CO_2, = 0,1158 C, and 0,1468 gr. H_2O = 0,0163 H.

Calculated for $C_{10}H_{17}O(C_2H_3O)$		Found	
		I	II
C_{12} 144	73,47 %	73,03 %	73,20 %
H_{20} 20	10,20 %	10,33 %	10,30 %
O_2 32	16,33 %		
196	100,00		

These results are seen to accord quite closely with the theory.

This compound ether was then saponified by alcoholic potassa, the alcohol first distilled off from the water

bath, water then added, and the distillation continued until oil drops ceased to pass with the aqueous vapour The Asarol thus collected was found to possess all of its original properties. The contents of the flask were then acidulated with dilute sulphuric acid, and distilled until the distillate no longer showed a decided acid reaction.The acid was then converted by means of barium carbonate into the barium salt, the solution of which afforded upon evaporation a group of crystals, which were analysed with the following result.

0,6864 gr. of the salt, dried at 105—110° c. until of constant weight, gave 0,6260 gr. Ba SO_4 = 0,3680 Ba.

Calculated for Ba $(C_2 H_3 O_2)$ 2	Found
Ba 53,73 %	53,61 %

I afterwards sought to prepare the benzoic ether of the Asarol, in the hope that this might be solid and crystallizable.

To this purpose the Asarol was mixed with benzoyl chloride in molecular proportions, and the mixture heated in a flask provided with an inverted condenser upon the sand bath for about six hours. The reaction in the beginning was quite energetic, with evolution of HCl vapours, and, upon cooling, the contents of the flask solidified to a compact mass of acicular crystals. These were purified by repeated crystallization from petroleum benzine, in order to avoid any possibility of decomposition by contact with aqueous liquids. Long colorless, needle shaped crystals were thus obtained, which were at first supposed to be the benzoic ether, produced according to the following reaction

$$C_{10} H_{17} - O H + C_6 H_5 - CO Cl = C_{10} H_{17} - O - CO - C_6 H_5 + H Cl.$$

The melting point was determined and found to agree exactly with that of benzoic acid, and of which it alone con-

sisted, as upon saponification it yielded not a trace of Asarol. The reaction had thus assumed another phase, and may perhaps be expressed by the equation :

$$C_{10}H_{17} - OH + C_6H_5 - CO\,Cl = C_6H_5 - COOH + C_{10}H_{16} + HCl,$$

or the compound ether, if first formed, having been afterwards split into benzoic acid and a terpene.

Another attempt was made to obtain the ether in question, according to the method of Berthelot[1], who says of the «Camphol benzoïque» : «Ce corps se prépare en chauffant l'acide benzoïque avec le camphol à 200 degrés pendant huit à dix heures. On sépare l'excès d'acide benzoïque par le carbonate de potasse, et la potasse, comme il a été dit à la cholesterine benzoïque, puis l'excès de camphol, en suivant la même marche que pour le camphol stéarique. On obtient une huile neutre, incolore, inodore, soluble dans l'éther et même dans l'alcool froid. Chauffé à 120 degrés avec la chaux sodée, le camphol benzoïque régénère rapidement le camphol qui se sublime, et l'acide benzoïque qui demeure uni à l'alcali.»

With the process here given, or even when modified in various ways, I have ben equally unsuccessful in obtaining the benzoic ether. That it is really formed by these reactions there can be no doubt, but as prepared from the Asarol it is a very unstable compound, and was found to be invariably decomposed by heating, or by distillation, into a terpene, with the separation of benzoic acid.

It seems also quite uncertain as to whether the body described by Berthelot was a definite chemical compound, as its boiling point is not mentioned, and no analysis appears to have been made of it. It is also remarkable that as

---

1. Ann. de chimie et de physique. 1859, t. LVI, p. 92.

prepared from the solid borneol it should be so stable a compound as to resist the treatment with potassium carbonate and potassa, as described, without undergoing decomposition.

The terpene which I have obtained by this reaction was found to distill quite constant at about 170° c., and was submitted to analysis with the following result :

0,2132 gr. of substance gave 0,6864 gr. CO_2 = 0,1872 C. and 0,2300 gr. H_2O = 0,0255 H.

Calculated for $C_{10}H_{16}$			Found
C_{10}	120	88,24%	87,80%
H_{16}	16	11,76%	11,96%
	136	100,00	99,76

It is a bright and colorless liquid, possessing an agreeable lemon like odor. Its specific gravity is 0,828 at 12° c., and is opticelly inactive, thus agreeing with the terpene pre-existing in the oil.

Attention has been called by Wright[1] to an interesting reaction observed with the citronnellol of citronella oil, by which the dibromide, upon heating, is decomposed with the formation of cymol :

$$C_{10}H_{18}Br_2O = H_2O + 2HBr + C_{10}H_{14}.$$

I have repeated the same experiment with the Asarol of Asarum oil, but was unable to isolate the cymol from the exceedingly large amount of tarry matters which were formed by the reaction.

By the action of phosphorous pentachloride upon the Asarol, at ordinary temperatures or in the cold, or by heating the Asarol with ten times its weight of fuming hydrochloric acid in a sealed tube for ten hours, I was unable to

1. Journ. chem. Soc., 1874, p. 323.

obtain the crystallizable chloride, $C_{10}H_{17}Cl$, which was first formed by Berthelot[1] from Borneo camphor; dark colored, viscid liquids being formed, having a strongly camphoraceous odor, but which were not considered sufficiently pure for analysis. Kachler[2] has also shown that the crystallizable chloride is a very unstable compound, losing a part of its chlorine by simply drying over sulphuric acid.

Upon warming the Asarol for several hours with phosphoric anhydride, water is readily abstracted from the molecule, and it is resolved into a terpene, corresponding to the socalled *Borneene,* and which may be designated as *Asarene.*

The product, after rectification over metallic sodium, was found to distill quite constant at about 170° c. It was analysed with the following result:

0,2410 gr. of substance gave 0,7756 gr. $CO_2 = 0{,}2115$ C, and 0,2562 gr. $H_2O = 0{,}0285$ H.

Calculated for $C_{10}H_{16}$			Found
C_{10}	120	88,24%	87,76%
H_{16}	16	11,76%	11,82%
	136	100,00	99,58

This liquid has an agreeable, lemon like odor, Its specific gravity is 0,884 at 11° c.

The Asarol when submitted to oxydation with nitric acid, either concentrated or dilute, is converted into a dark colored, resinous substance, readily soluble in alkalies, and possibly the so-called «camphresic acid» of Schwanert, but from which no crystallizable acid could be obtained.

---

1. Ann. de chimie et de physique. 1859, t. LVI, p. 92.
2. Liebig's Annalen, Bd. 197, p. 86.

III. Fraction 222° — 226° c. (Corr.).

This is a colorless, fragrant liquid, and was submitted to analysis with the following result:

(I) 0,2320 gr. of substance gave 0,6576 gr. CO_2 = 0,1793 C, and 0,2420 gr. H_2O = 0,0269 H.

(II) 0,2734 gr. gave 0,7784 gr. CO_2 = 0,2123 C, and 0,2848 gr. H_2O = 0,0316 H.

Calculated for $C_{10}H_{18}O$			Found	
			I	II
C_{10}	120	77,92 %	77,30 %	77,65 %
H_{18}	18	11,69 %	11,60 %	11,56 %
O	16	10,39 %		
	154	100,00		

This fraction, although boiling 25 degrees higher than the preceeding, is seen to consist of a body isomeric with Asarol. Its odor is however quite distinct, reminding more of the oil of *Pelargonium roseum*, the so called rose geranium, and differs also in its behavior towards polarized light; its rotation in sodium light in a column of 100 mm, being — 7°,2 at 15° c, Its specific gravity is 0,919 at 10° c.

A determination of its vapour density, made according to the new method of Victor Meyer [1], with the employment of a paraffine bath, gave the following numbers. The temperature of the bath being maintained constant at 316° c. :

S = The weight of substance employed = 0,0706 gr.

t = The temperature of the water in the cylinder = 22°,5 c.

B = The barometric pressure, reduced to 0° c. = 750,6 mm.

w = The tension of aqueous vapour at the temperature $t°$, = 20,3 mm.

V = The measured volume of air = 11,6 ccm.

1. Ber. d. deutsch. chem. Ges., XI, p. 2253.

Inserting these factors in the following formula:

$$D = \frac{S\ (1 + 0{,}003665,\ t)\ 587780}{(B - w)\ V}$$

we obtain for D the value *5,30,* in very close accordance with the theoretical value, or *5,33.*

The chemical behavior of this fraction is perfectly analogous to the preceeding, so that it is unnecessary to repeat the reactions already detailed. Nitric acid having been found an unsuitable oxydizing agent for the Asarol, as shown by the behavior of the preceeding fraction, I have employed in this instance the chromic acid mixture, and in the proportions employed by Fittig for the oxydation of the terpenes. The oxydation proceeded quictly, with the evolution of a small amount of carbonic acid gas, and after a few hours the conversion of the liquid into ordinary camphor was observed. This latter was at once recognized by its powerful odor, as well as by the small crystalline flakes, undoubtedly of that substance, which were found floating on the surface of the liquid. The amount of camphor, however, appearing to small to separate, the oxydation was continued, and after two days boiling the oil had entirely disappeared.

The product was then distilled, in order to separate the volatile acid, and the remaining green chromic liquor shaken with ether. The volatile acid was converted into the barium salt, and found to be simply acetic acid, as seen from the following analysis :

0,7656 gr. of the salt lost by drying at 105—110° c., until of constant weight 0,0518 gr. H_2O, and gave 0,6452 gr. $BaSO_4$ = 0,3793 Ba.

Calculated for $Ba(C_2H_3O_2)_2 + H_2O$		Found
Ba	50,18 %	49,54 %
H_2O	6,60 %	6,76 %

From the chromic liquor, after the separation of the acetic acid, another acid, not volatile with aqueous vapour, was extracted by means of ether. It separated from the concentrated aqueous solution as a compact mass of crystals, appearing to be perfectly homogenous, but without special form. The acid is very freely soluble in water, alcohol, and ether, and is also somewhat hygroscopic, in consequence of which I was unable to determine its melting point with accuracy.

The acid was dried over sulphuric acid until of constant weight, and then submitted to analysis :

(I) 0,2738 gr. of acid gave 0,5398 gr. Co_2 = 0,1472 C, and 0,1684 gr. H_2O = 0,0187 H.

(II) 0,2774 gr. of acid gave 0,5422 gr. Co_2 = 0,1479 C, and 0,1694 gr. H_2O = 0,0188 H.

Calculated for $C_9 H_{12} O_5$		Found	
		I	II
C 9 108	54,00%	53,72%	53,32%
H_{12} 12	6,00%	6,83%	6,78%
O 80	40,00%		
200	100,00		

This acid is perhaps identical with the tribasic camphoronic acid of Kachler[1], which it resembles in most of its properties, and which is formed by the oxydation of camphor and analogous substances.

Kachler has also shown the so-called «camphresic acid» of Schwanert[2] to consist essentially of the crystallizable camphoronic acid, and to which the above formula has been assigned.

---

1. Liebig's Annalen, Bd. 159, p. 289.
2. Ibid., Bd. 128, p. 77

I have been unable as yet, on account of the limited amount of material, to establish the probable identity of these two acids.

IV. Fraction 254³ — 257⁵° c. (Corr.).

This is a colorless, viscid, neutral liquid and possesses no special odor. It is somewhat heavier than water, and sinks in that liquid; its specific gravity is 1,021 at 12° c., and is optically inactive. Exposed to a temperature of —27° c., it became somewhat more viscid, but without the separation of any crystalline matter. It was submitted to analysis with the following result :

(I) 0,3374 gr. of substance gave 0,9224 gr. CO_2 = 0,2516 C, and 0,2580 gr. H_2O = 0,0287 H.

(II) 0,2436 gr. gave 0,6648 gr. CO_2 = 0,1813 C, and 0,1868 gr. H_2O = 0,0207 H

Calculated for $C_{12}H_{16}O_2$			Found	
			I	II
C_{12}	144	75,00 %	74,57 %	74,42 %
H_{16}	16	8,33 %	8,50 %	8,41 %
O_2	32	16,67 %		
	192	100,00		

The correctness of this empirical formula is confirmed by two determinations of its vapour density, made according to the new method of Victor Meyer, with the employment of a paraffine bath, instead of lead, in order to avoid decomposition by excessive heat. To Professor Kundt, Director of the Physical Laboratory, I desire here to express my thanks for having kindly placed the necessary apparatus for these determinations at my service.

I.

The temperature of the bath was observed at 307° c.

S = The weight of substance employed = 0,0792 gr.
t = The temperature of the water in the cylinder = 20°,5 c.
B = The barometric pressure, reduced to 0° c. = 749,8 mm.
w = The tension of aqueous vapour at the temperature $t°$, = 17,9 mm.
V = The measured volume of air = 11,6 C, cm.

The vapour density is then, deducted from the following formula :

$$D = \frac{S\,(1 + 0{,}003665,\ t)\ 587780}{(B - w)\ V}$$

$$D = 5{,}89$$

II.

The temperature of the bath was observed at 312° c.

The figures obtained may be represented by the preceeding factors.

S = 0,0812 gr.
t = 21,0° c.
B = 749,8 mm.
w = 18,5 mm.
V = 11,6 C, cm.

$$D = \frac{S\,(1 + 0{,}003665,\ t)\ 587780}{(B - w)\ V}$$

$$D = 6{,}06$$

Calculated for $C_{12}\,H_{16}\,O_2$	Found	
	I	II
Vapour density 6,65	5,89	6,06

This body is quite indifferent in its chemical behavior. Having been obtained by distillation from a strongly alkaline liquid, it is excluded from the class of phenols, and is also incapable of combining with alkaline bisulphites.

Assuming the possibility of its playing the part of a diatomic alcohol, it was heated for about five hours with acetic anhydride, in the proportion of one molecule of substance to two of anhydride, but no compound ether was thus formed.

Treated with metallic sodium it was impossible to obtain any hydrocarbon therefrom; the sodium dissolving therein by gentle heating to form a gelatinous mass, which upon further heating became darkly colored and decomposed.

Fuming hydrochloric acid imparts to the liquid a most intense and permanent carmine red coloration, and with bromine it assumes a deep violet color, but appears to form no definite compounds therewith.

Concentrated sulphuric acid dissolves it in the cold with evolution of sulphurous acid, and the solution acquires an intense blood red coloration. A sulphonic acid is thus formed, in which apparently one H atom is replaced by the sulpho group, $SO^2 — OH$.

The acid thus obtained was dissolved in water, a small amount of resinous matter remaining undissolved, and the clear, reddish colored liquid treated with carbonate of barium, filtered and evaporated. The barium salt was thus obtained in the form of small, colorless, crystalline scales, freely soluble in water.

0,3528 gr. of the air dried salt lost upon drying at 105—110° c. 0,0122 gr. H_2O, and gave 0,1212 gr. $BaSo_4$ = 0,0712 Ba.

Calculated for Ba $(C_{12}H_{15}O_2—SO_3)_2 + 1^1/_2 H_2O$		Found
Ba	19,40 %	20,18 %
H_2O	3,82 %	3,46 %

The aqueous solution of the salt strikes no coloration with ferric chloride.

The oily liquid is violently attacked by concentrated nitric acid, even in the cold, with evolution of nitric oxide vapours, and imparts to the liquid a blood red coloration, Amorphous nitro products appear thereby to be first formed, and, upon gently warming, it is converted into oxalic acid.

By oxydation with the chromic acid mixture a copious evolution of carbonic acid gas was observed; the only volatile acid formed being acetic acid, as seen from the analysis of the silver salt.

0, 1338 gr. of the salt, dried over sulphuric acid until of constant weight, gave upon ignition 0,0860 gr. metallic silver.

Calculated for Ag. $C_2H_3O_2$	Found
Ag 64,67 %	64,27 %

From the chromic liquor, by extraction with ether, a small amount of a crystallizable acid was obtained, the melting point of which was observed at 171—172° c. It is sparingly soluble in cold water, more readily in hot water, from which it crystallizes upon cooling, and is quite freely soluble in alcohol and ether.

0,1892 gr. of acid, dried at 100° c. until of constant weight, gave 0,4118 gr. $Co_2 = 0,1123$ C, and 0,1024 gr. $H_2O = 0,0114$ H, or 59,35 % C, and 6,02 % H.

The formula $C_9H_{10}O_4$ would require 59,34 % C, and 5,49 % H.

The amount of this acid obtained was simply sufficient for one analysis, so that it was impossible to confirm the correctness of this result.

It is a very interesting fact that this neutral and quite indifferent body, whose general chemical characters have just been described, and which is contained in the oil in considerable amount, is isomeric with the crystalline compound *Helenin*, isolated by Kallen [1] from the root of *Inula Helenium*, L.; the same chemist having shown that the Helenin or Alant camphor of the older chemists [2] is not a simple body, but a mixture of Alant camphor or *Alantol* $C_{10}H_{16}O$, *Alantic anhydride*, and a body for which the name of Helenin is now reserved.

The empirical formula assigned by Kallen to Helenin is C_6H_8O, but there is no doubt that the molecular formula is a multiple of these numbers, and would be found te agree with the formula $C_{12}H_{16}O_2$, although, as it suffers decomposition by conversion into vapour, this question cannot be directly decided.

The reactions of the body contained in Asarum oil are further in many respects quite analogous to those of Helenin, and of which it would appear to be simply a liquid modification.

The occurrence of these two bodies in plants botanically so widely separated is by no means surprising, when we consider the wide distribution of bodies isomeric with borneol, and the occurrence of the latter in a crystalline form in the composite plant, *Blumea balsamifera* forming the *Ngai* camphor of the chinese.

V. Fraction 275 — 350° c.

This intensely blue colored oil is a viscid liquid of empyreumatic odor, and possesses no constant boiling point.

---

1. Ber. d. deutsch. chem. Ges., 1873, p. 1506; ibid., 1876, p. 154.
2. Gmelin's Handbuch d. Chemie, 1866, Bd. IV, p. 1914.

It is the so-called «*Azulene*» of Piesse, and the «*Coerulene*» of Gladstone.

Its density is about the same as that of water; its specific gravity being 1,002 at 8° c. The oil diluted with alcohol, and examined by the spectroscope, shows no other optical behavior than that which would naturally be presupposed, viz. the perfect absorbtion of the yellow rays, forming a dark band in the spectrum. The same behavior is shown by the blue oil of galbanum, as also by a solution of indigo.

Similar blue colored bodies have been observed as yet to be obtainable from the oils furnished by the following plants; from the flowers of *Matricaria Chamomilla,* L., *Anthemis nobilis,* L., and *Arnica montana,* L., from the rhizome of *Acorus Calamus,* L., and the roots of *Valeriana officinalis,* L., and *Ferula Sumbul,* Hooker; from the seeds of *Nectandra Puchury,* and the herbs *Pelargonium roseum,* and *Pogostemon Patchouli,* Pelletier; further in a marked degree by the dry distillation of the resins of galbanum and Asafœtida, and from the so-called aromatic guaiac resin (Resina Guaiaci Peruviana aromatica vel odorata). As to the nature of the coloring principle contained in the oils here enumerated, we have as yet but little knowledge, and their analysis gives us but an inperfect idea of their chemical composition, although several seem to correspond to the empirical formula $C_{20} H_{30} O$, and are stated to be convertable by the action of metallic sodium into an hydrocarbon of the composition $C_{40} H_{15}$.

That they are mixed and complicated bodies is evident from the inconstancy of their boiling points, while their usually viscid character, and partial decomposition resulting from the high temperature necessary for their distillation, renders it difficult to obtain any definite body therefrom.

For those interested in the literature of the blue oils, reference may be made to the following papers.

Liebig's Annalen. Bd, 49, p, 243; Bd. 119, p. 262.
Archiv der Pharm., Bd. 209 (1876), p. 193.
Ber. d. deutsch. chem. Ges., 1871, p. 37, 1873, p. 1210.

Acids obtained by the saponification of the oil.

The alkaline liquid remaining after saponification, and the separation of the oil by distillation, was acidulated with dilute sulphuric acid and distilled; fresh portions of water being from time to time added, and the distillation continued until the distilled liquid no longer showed a decided acid reaction.

A colorless, strongly acid liquid of a peculiar, unpleasant odor was thus obtained, containing a small amount of an acid in the form of yellowish, oily drops, floating upon the over surface, but which finally became dissolved. The entire amount of liquid was then carefully neutralized by a dilute solution of sodium hydrate, and evaporated. The sodium salt, although having been found to consist chiefly of acetate, refused to crystallize, in consequence of the presence of another acid forming a deliquescent salt, It was then again super saturated with dilute sulphuric acid, and shaken with ether. The etherial solution was allowed to evaporate upon the surface of a small amount of water, which absorbed the acetic acid, while the other acid was obtained as an oily liquid, sparingly soluble in water.

The acetic acid was again converted into the sodium salt, which was now obtained in the characteristic prismatic crystals ol sodium acetate.

From the sodium salt the silver salt was prepared, by means of a solution of silver nitrate.

0,1944 gr. of the silver salt, dried over sulphuric acid until of constant weight, gave upon ignition 0,1248 gr. metallic silver

Calculated for $Ag\ C_2 H_3 O_2$		Found
Ag	64,67 %	64,20 %

The barium salt was prepared from the pure acid by digestion with barium carbonate. Upon evaporation of the solution a group of large compact crystals was first formed, which were removed, and by further evaporation an additional quantity of prismatic crystals was obtained. These two salts were each analysed with the following result.

(I. crystallization) 0,5970 gr. of the salt lost upon drying at 105—110° c. until of constant weight, 0,0215 gr H_2O, and gave 0,5236 gr. $Ba\ So_4$ = 0,3078 Ba.

Calculated for $Ba\ (C_2 H_3 O_2)_2 + {}^1/_2\ H_2 O$		Found
Ba	51,89 %	51,56 %
${}^1/_2 H_2 O$	3,41 %	3,60 %

(II. crystallizations) 0,6555 gr. of the salt lost upon drying at 105—110° c. until of constant weight, 0,0455 gr H_2O, and gave 0,5566 gr. $Ba\ So_4$ = 0,3272 Ba.

Calculated for $Ba\ (C_2 H_3 O_2)_2 + H_2 O$		Found
Ba	50,18 %	49,91 %
H_2O	6,60 %	6,94 %

The oily acid was afterwards converted into the sodium salt, and found to be deliquescent and incapable of crystallizing.

From the sodium salt I afterwards prepared the copper salt, by precipitation with a solution of cupric acetate, It was thus obtained in the form of a light green, flocculent precipitate, quite insoluble in cold water, but readily soluble in warm alcohol, forming a solution of a bright emerald

green color, from which however I could not obtain it in a crystalline form.

The copper salt was then dried at 100° c. until of constant weight, and submitted to analysis with the following result :

I. 0,3114 gr. of the salt gave upon ignition 0,0902 gr. Cu O = 0,0720 Cu.

II. 0,2304 gr. of the salt gave upon combustion with oxide of copper 0,3806 gr. Co_2 = 0,1038 C, and 0,1466 gr. H_2O = 0,0163 H.

Calculated for Cu $(C_5 H_9 O_2)_2$			Found	
			I	II
Cu	63,4	23,88 %	23,12 %	—
C_{10}	120,	45,22 %	—	45,05 %
H_{18}	18,	6,78 %	—	7,07 %
O_4	64,	24,12 %	—	—
	265,4	100,00		

The acid contained in the oil is thus principally acetic acid, associated as it would appear with a very small amount of valerianic acid.

They are also contained therein in the form of compound ethers, and forming the principal constituents of the oil; as it has been previously shown that the original oil is quite neutral in its action upon litmus, and can therefore contain no free acids.

To briefly summarize the results of the researches previously detailed, it is seen that the volatile oil of Asarum Canadense consists of the following components :

I. A very small amount of a terpene $C_{10} H_{16}$, or *Asarene*.

II. The acetic ether of an alcohol isomeric with borneol, and which may be designated as *Asarol*.

The Asarol is also present in the oil in two modifications, differing however considerably in their boiling points, and in their behavior towards polarized light.

III. Apparently a small amount of the valerianic ether of Asarol.

IV. An indifferent, neutral body of undetermined constitution, and having the empirical formula $C_{42} H_{16} O_2$.

This body from its analogy with Helenin may properly be designated as *Asarin*, but should then not be confoundet with the so-called Asarum camphor, or other indefinite bodies which have received the same appellation.

V. A small amount of a deeply blue colored oil, the so-called *Azulene* or *Coerulene*.

Typ. et Lith. A. Dusch, r. des Tanneurs. 26. Strasbourg.